DIRECT METHANATION – A NEW METHOD OF CONVERTING SYNTHESIS GAS TO SUBSTITUTE NATURAL GAS

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I. INTRODUCTION

The United States has vast resources of energy in the form of coal. One method of distributing this energy source to the consumer is to gasify the coal and distribute the gas through the existing natural gas pipeline distribution system. However, raw synthesis gas from a coal gasifier is not of sufficient purity and does not provide heating value suitable for use directly as substitute natural gas (SNG). The synthesis gas produced by a coal gasifier requires extensive purification and upgrading before it can be interchanged with natural gas. The current raw gas conversion systems were not specifically designed with the production of pipeline quality gas from coal in mind. Potentially, significant cost reductions could result from the development of an improved, integrated processing system.

As part of the strategic objective of improving reliability, operability, or reducing gas costs of coal gasification processes, the Gas Research Institute (GRI) is developing a new process for converting synthesis gas to SNG. The key to this process is the development of a sulfur-resistant, direct methanation catalyst. Preliminary cost estimates show that the direct methanation process could decrease capital costs by over 20% and operating costs by 10%, resulting in gas costs savings of about 15% over state-of-the-art methanation and combined shift-methanation processes.

II. METHANATION PROCESSES

A conventional gas processing system, as shown in Figure 1A, includes gas quench, water-gas shift, gas cooling, acid gas removal, methanation, dehydration, and compression. These clean-up processes produce separate streams that require further purification so that by-products, such as sulfur, phenols, ammonia, BTX, and tars, can be isolated for sale whenever possible. The gas quench utilizes oil and/or water to cool the raw gas and to remove particulates, tars, and oils, and other condensible components.

Water-gas shift (Equation 1) is required to adjust the H_2/CO ratio to over 3

$$CO + H_2O \rightleftharpoons H_2 + CO_2 \qquad 1)$$
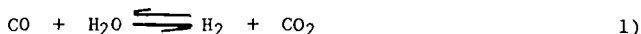
as needed for methanation. Added steam reacts with the carbon monoxide to produce the required hydrogen. The use of new sulfur-insensitive shift catalysts show an economic advantage by allowing the shift process to be upstream of the gas cooling and acid gas removal systems. The acid gas removal system removes water, carbon dioxide, and sulfur-containing compounds. The current methanation process uses nickel-based catalysts for

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converting (methanating) carbon monoxide and hydrogen to methane (Equation 2). After methanation, dehydration is required to remove the water formed during methanation; after which the gas is compressed to pipeline standards.

$$3H_2 + CO \rightleftharpoons CH_4 + H_2O \qquad\qquad 2)$$
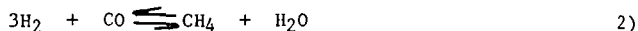
Nickel catalysts have demonstrated their effectiveness for converting synthesis gas to methane. However, there are very strict process restrictions for successful use of nickel catalysts. Satisfying these restrictions can require process steps that are costly. A major restriction of nickel catalysts arises from their extreme sensitivity to poisoning by sulfur compounds that are always present in coal-derived synthesis gas. Although "sweet" pipeline gas can contain 4 ppm hydrogen sulfide (0.25 grains/100 scf), gas processed by nickel catalysts must be purified to 0.1 ppm sulfur to avoid irreversible poisoning of the catalyst. The nickel catalyst can also be irreversibly poisoned by carbon fouling, unless the hydrogen/carbon monoxide ratio of the input gas is maintained above 2.85 and/or excess steam is added. Nickel catalysts are also deactivated at high temperatures (above 950°F), such as those that can occur during the exothermic methantion reaction. Nickel catalysts cannot be exposed to oxygen after activation. They require special handling and pretreatment procedures to maintain reactivity.

Improvements to the conventional methanation process are those embodying combined shift-methanation, such as those developed by Conoco, R. M. Parsons, United Catalyst, ICI, and UOP. These processes utilize the water formed in methanation for water-gas shift. (Equations 1 and 2 simultaneously.) A combined shift-methanation process is shown in Figure 1B. Since nickel-based catalysts are used, removal of sulfur is required prior to shift-methanation. All the combined shift-methanation processes require steam addition for stoichiometry, temperature moderation, and/or to prevent carbon formation. An additional acid gas removal system is required downstream of the shift-methanation process to remove the high concentration of CO_2.

The direct methanation process being developed for GRI shows significant improvements over the conventional methanation and combined shift-methanation processes. The direct methanation process, shown in Figure 1C, methanates the raw gas directly using equal molar concentrations of carbon monoxide and hydrogen to form carbon dioxide and water. The chemistry of the process is such that steam is not needed either to suppress carbon formation or to drive the water-gas shift reaction. Although the overall reaction for combined shift-methanation is the same as for direct methanation (Equation 3), the mech-

$$2CO + 2H_2 \rightleftharpoons CH_4 + CO_2 \qquad\qquad 3)$$
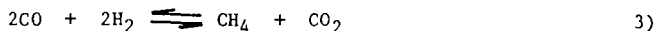
anism appears different in that CO_2 is produced directly rather than by the water-gas shift, thus eliminating the high steam requirement. The process shows potential savings in steam usage and acid gas removal. Other process advantages are expanded upon in the remainder of the paper.

III. DIRECT METHANATION CATALYST DEVELOPMENT

Catalysis Research Corporation (CRC), located in Palisades Park, New Jersey, is responsible for iteratively developing novel catalyst formulations, performing scoping tests to evaluate the effectiveness of the formulations, and proposing process sequences that best utilize the advantages of the most promising catalysts. During the last six years, CRC has tested over 600 new catalyst formulations resulting in several compositions that have promise for application both in a conventional methanation process and in a new direct methanation process.

The catalyst development program for a sulfur-resistant methanation catalyst, from 1974-1978, lead to two patented catalyst formulations. In 1977, Patent 4,151,191 was issued to CRC for a cerium-molybdenum catalyst, designated as GRI Series 200 (GRI-C-284). In 1981, Patent 4,260,553 was issued to CRC for a cerium-molybdenum-aluminium catalyst, designated as GRI Series 300 (GRI-C-318). Both patents were assigned to GRI. These catalysts satisfied the original project objective of developing a sulfur-resistant methanation catalyst; however, they also lead to a new area of study.

In 1979, a second breakthrough was made in the CRC catalyst formulation work. A new family of catalysts, the GRI Series 400 and 500 catalysts, were developed that promote the direct methanation reaction (Equation 3) rather than the water-gas shift reaction (Equation 1). These catalysts provide the key to the new direct methanation process. The overall project objective was changed to reflect this breakthrough, and subsequential work concentrated on developing a direct methanation process.

The present series of catalysts are the most active catalysts yet developed. These catalysts show sufficiently high conversion and selectivity such that they can be used in a direct methanation process that involves no gas recycling and uses only a single acid gas removal system. They can operate with feed gases containing high levels of sulfur compounds and CO_2. Carbon formation has not been observed, even with H_2/CO ratios as low as 0.1 and with no steam addition, and the catalysts have high maximum operating temperatures. The catalyst are very easy to handle; they can be exposed to air at room temperature with no loss of activity, and therefore, they require little or no pretreatment.

IV. DIRECT METHANATION CATALYST CHARACTERIZATION

SRI International, located in Menlo Park, California, is responsible for characterizing the promising catalysts developed by CRC. The studies are intended to define the bulk and surface properties that affect the specific methanation activity, thermal stability, and deactivation resistance of these catalysts as an aid in further development and improvement. SRI has been involved with the Direct Methanation Project since 1977, but also has developed catalysts under contracts to the American Gas Association (A.G.A.) since 1972.

The direct methanation process requires a catalyst that selectively promotes the direct methanation reaction (Equation 3). Catalyst selectivity and activity can be strongly dependent upon both the composition and morphology of the catalyst. Development of basic methods to relate microcompositional and morphological properties of the catalyst to selectivity and activity is vitally important in the development of improved catalysts and gas processes for coal conversion plants. Work being performed by SRI is intended to refine measurement techniques suitable for understanding the observed behavior of the direct methanation catalysts.

In order to evaluate catalyst structure, SRI had to develop or improve new experimental techniques utilizing (1) x-ray photoelectron spectroscopy (XPS or ESCA), (2) scanning electron microscopy (SEM), and (3) BET surface area measurements to provide information on structural changes of catalysts. Dispersion and sintering stability studies have been performed using x-ray diffraction (XRD), SEM, and ESCA to define changes in the properties that control methanation activity. Solid state properties of the catalysts have been determined by a variety of surface science techniques.

Because of its nature, most of the work performed by SRI is proprietary; a general discussion of some aspects of the work follows. First, tests were

performed to study structural changes of the catalyst during methanation. This resulted in the discovery of a critical formulation variable that controls the specific methanation activity. Later, discovery of a correlation between methanation activity and surface acidity, as measured by quantitative absorption of a weak base (ammonia), simplified catalyst evaluation. Finally, a preliminary explanation of the mechanism by which the GRI Series 400 and 500 catalysts operate was developed.

V. DIRECT CATALYST METHANATION EVALUATION

The Institute of Gas Technology (IGT), located in Chicago, Illinois, is responsible for evaluating the promising catalyst formulations prepared by CRC using feed gases that simulate gasifier effuents and developing the process design data for promising catalysts in various processing sequences. The studies are intended to test the catalysts for longer times and at more severe and realistic conditions than the scoping tests performed by CRC. IGT has been involved with the Direct Methanation Project since 1978, but also has evaluated catalyst under contracts to A.G.A. since 1972.

The GRI Series 500 catalysts are the best methanation catalysts tested to date. They are capable of promoting the methanation reaction at temperatures from 600° to $1200^{\circ}F$, at all pressures from 200 to 1000 psig, at feed gas H_2/CO mole ratios from 3 down to 0.5, and in the presence of up to 3 mole % sulfur (H_2S, COS, CS_2, CH_3SH, C_2H_5SH, C_3H_7SH, and C_4H_4S). No carbon formation was detected under any of the above mentioned conditions. The presence of CO_2 in the feed retarded the total CO conversion but did not promote any other reactions. Hydrocarbon additions of up to 2 mole % C_6H_6, 0.05 mole % C_6H_5OH, and 0.3 mole % NH_3 did not poison or foul the catalysts. Life tests were conducted on the GRI Series 200 catalysts for more than 5000 hours, and ongoing life tests of the GRI Series 500 catalysts have extended for more than 2500 hours.

The promising catalysts were also tested in various processing sequences to provide process design data. IGT tested the effects of space velocity, temperature, pressure, and feed composition on the conversion of CO and H_2 to CH_4 and CO_2 by the direct methanation process. The feed gas simulated a gasifier effluent. The product composition of each reactor was used as the feed composition for each successive reactor stage, and runs at identical temperature and pressure were conducted. This approach generated information on the process variables at each reactor stage, provided input for process design, and served as a guideline for catalyst improvement.

Quench gases simulating those from the dry-bottom Lurgi, Slagging Lurgi, Westinghouse and HYGAS processes were tested. For cases where the H_2/CO ratio is less than 1, as in the Slagging Lurgi case at $H_2/CO = 0.4$, a preconditioning shift was required to increase the H_2/CO ratio to 1.1 to 1.3. The process steam requirements are therefore much lower than required for shifting the gas to 3 as needed for nickel methanation catalysts. The shift was performed with a CRC developed, GRI Series 300 catalyst and required only 16% steam in the feed gas to the methanation step, as shown in Figure 2. Typical data for a Slagging Lurgi flowsheet are shown in Figure 3 for the first reactor stage.

VI. DIRECT PROCESS METHANATION EVALUATION

C F Braun & Company, located in Alhambra, California, is the engineering/construction firm responsible for developing conceptual processes from the design data collected by IGT and from the process sequences recommended by CRC. First-cut economic evaluations are then performed based on the conceptual process design. The conceptual process design work includes

preparing process flow diagrams and sizing equipment. Capital cost and operating requirements estimates are used in the economic evaluation to determine gas costs.

A preliminary economic evaluation was conducted in 1979, based on the use of a GRI Series 300 catalyst. The results indicated the concept would not be competitive because the design required CO_2 removal prior to methanation. However, CO_2 removal is not required with the use of the GRI Series 400 and 500 catalysts, because these catalysts have good activity in streams with a high CO_2 content.

A first-cut analysis of the direct methanation process for a Slagging Lurgi gasifier raw gas was just completed. The analysis compared a 250 billion Btu/day Slagging Lurgi gasification plant with a combined shift-methanation process to a plant designed around the direct methanation process. The design of the gasifier was not changed, but the overall downstream process, utilizing commercially available subsystems, was redesigned to best exploit the direct methanation process advantages. A simplified flowsheet, based on a GRI Series 500 catalyst, is shown in Figure 4.

The preliminary results show the direct methanation process could reduce capital costs over 20%, operating cost by 10%, and reduce the gas cost by about 15%. The savings are realized in reduced steam requirements and more efficient sulfur management processes specifically for this application. Further savings were anticipated when new subsystems are developed specifically for use with direct methanation.

VII. CONCLUSIONS

The current GRI project to develop a direct methanation process is making excellent technical progress. Direct methanation processes utilizing the CRC catalysts could potentially realize the following advantages over existing technology:
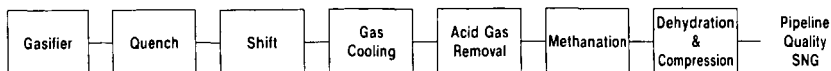
o   Reduced plant investment, operating costs, and gas costs
o   Effective hydrogen utilization
o   One acid gas removal step
o   Smaller acid gas removal feed stream
o   Higher energy efficiency
o   Sulfur tolerance
o   Carbon fouling tolerance
o   Lower process steam requirements
o   Decreased heat exchange area

If the development continues to be successful, the direct methanation process will be pursued through the pilot plant scale to provide the technology base required for commercial application.
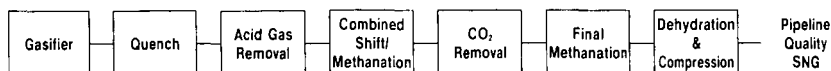
ACKNOWLEDGEMENT

A - CONVENTIONAL GAS PROCESSING SYSTEM

Gasifier — Quench — Shift — Gas Cooling — Acid Gas Removal — Methanation — Dehydration & Compression — Pipeline Quality SNG

B - COMBINED SHIFT/METHANATION GAS PROCESSING SYSTEM

Gasifier — Quench — Acid Gas Removal — Combined Shift/Methanation — CO_2 Removal — Final Methanation — Dehydration & Compression — Pipeline Quality SNG

C - DIRECT METHANATION GAS PROCESSING SYSTEM

Gasifier — Quench — Direct Methanation — Acid Gas Removal — Final Methanation — Dehydration & Compression — Pipeline Quality SNG

FIGURE 1. METHANATION PROCESSES

FEED COMP,
mol % (Water-Free)

CO	56.5
CO_2	3.4
H_2	29.0
CH_4	9.5
C_2H_6	0.05
C_3H_8	0.01
H_2S	1.0
N_2	0.45
TOTAL	100.00

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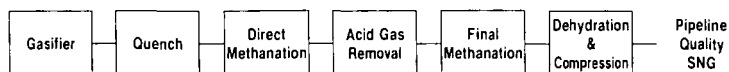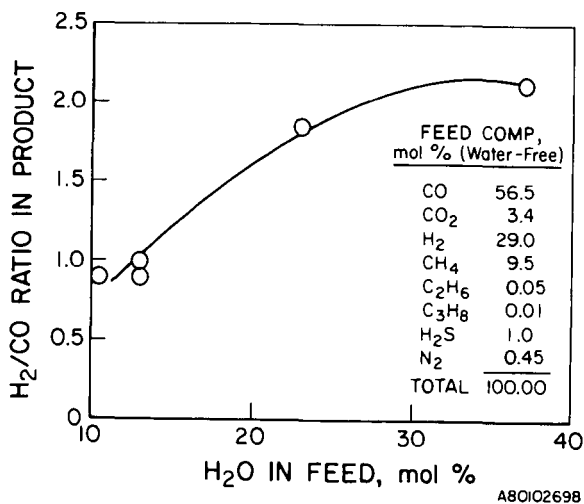
FIGURE 2. PRECONDITIONING SLAGGING LURGI
RAW GASES (1000 psig, 580°F, 4500 SCF/hr-ft^3
GRI-C-318 Catalyst)

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Feed composition table (right of chart):

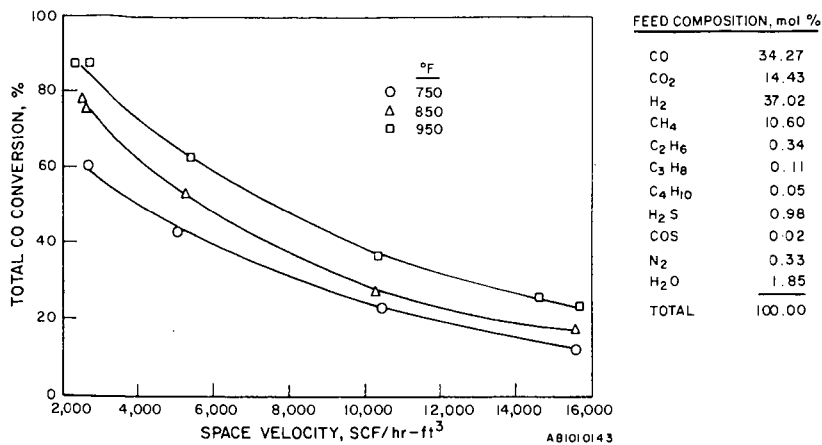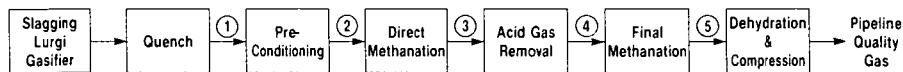| FEED COMPOSITION, mol %	
CO	34.27
CO_2	14.43
H_2	37.02
CH_4	10.60
C_2H_6	0.34
C_3H_8	0.11
C_4H_{10}	0.05
H_2S	0.98
COS	0.02
N_2	0.33
H_2O	1.85
TOTAL	100.00

FIGURE 3. CO CONVERSION IN THE FIRST DIRECT METHANATION STAGE FOR SLAGGING LURGI RAW GASES (450 psig, GRI-C-525 Catalyst)

Gas Analysis, Vol %
(H_2O and N_2 Free Basis)

Stream Component	①	②	③	④	⑤
CO	58.9	37.6	1.7	4.1	0.1
CO_2	6.5	19.1	56.1	0.7	0.8
H_2	25.9	35.8	6.7	16.1	4.7
CH_4	6.1	5.3	32.3	77.6	92.7
C_2^+	0.5	0.4	0.6	1.5	1.7
H_2S	2.1	1.8	2.6	0	0

FIGURE 4. CONCEPTUAL FLOWSHEET FOR DIRECT METHANATION OF SLAGGING LURGI RAW GASES

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